

# New version of the fluctuation Hamiltonian for liquids near the critical point

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## Abstract

We propose new canonical form of the fluctuational Hamiltonian which takes into account the fact that in the vicinity of the critical point there are two fluctuating fields. They are the field of the number density and the entropy. The proposed canonical form is based on the  $D_5$  catastrophe. In contrast to the standard approach of Landau-Ginzburg Hamiltonian which is based on  $A_3$  catastrophe the canonical form proposed for the fluctuational Hamiltonian naturally includes the asymmetric coupling between the fields.

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## 1. Introduction

The modern theory of the critical phenomena in liquids is based on the Landau-Ginsburg fluctuation Hamiltonian:

$$H_{LG}[\psi(\mathbf{r})] = \int d\mathbf{r} \left[ \frac{1}{2} (\nabla \psi(\mathbf{r}))^2 - h_\psi \psi(\mathbf{r}) + \frac{1}{2} r \psi^2(\mathbf{r}) + \frac{1}{4} g \psi^4(\mathbf{r}) \right], \quad (1)$$

where all designations are standard and the field  $\psi$  is normalized so that the coefficient at the square gradient is 1 [1, 2]. Such a form of the fluctuational Hamiltonian is sufficient to describe the critical asymptotical behavior of the free energy and is the basis for the isomorphism of such behavior with that of the Ising model. Nevertheless, the Hamiltonian lacks the asymmetrical terms which in general appear in the description of the molecular fluids [3, 4].

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The asymmetry of the coexistence curve (CC) is the characteristic feature for one-component liquids and solutions. It is absent in the Ising model and numerous lattice models. This circumstance indicates that the main role in the appearance of the asymmetry belongs to the effects of finite size for molecules of liquids.

The simplest characteristics of the asymmetry degree for the CC is its diameter defined as

$$\varphi_d = \frac{1}{2}(\varphi_l + \varphi_v), \quad (2)$$

where  $\varphi$  is the order parameter and subscripts  $l, g$  stand for the coexisting liquid and gas phases correspondingly. The latter can be identified with the extensive variable suitable to differentiate between the coexisting liquid and vapor phases. As rule, the main attention in literature is paid to the diameter of the CC in terms density-temperature. Its investigation has a long history.

In Pokrovskiy's work [5] (see also [6]) it was shown that the classical law of the rectilinear diameter [7, 8] is violated:

$$\tilde{n}_d = \frac{n_l + n_g}{2n_c} - 1 = D_{1-\alpha}|\tau|^{1-\alpha} + D_1|\tau| + \dots, \quad (3)$$

where  $n$  is the number density,  $\alpha$  is the critical exponent for the heat capacity. The new term in Eq. (3) is caused by the fluctuation effects. In accordance with [1] this contribution is connected with the non-orthogonality of the fluctuations of the density and the energy. From another point of view it means that the expansion of the density fluctuations with respect to the algebra of strongly fluctuating variables takes the form (see [1]):

$$\tilde{n} = \hat{A}_1 + \lambda \hat{A}_2 + \dots \quad (4)$$

Since  $\langle \hat{A}_1 \rangle = \pm a_1|\tau|^\beta$  (different signs correspond to the liquid and vapor branches of the CC) and  $\langle \hat{A}_2 \rangle = a_2|\tau|^{1-\alpha}$ , the expansion Eq. (4) directly to Eq. (3). For laboratory order parameter, which in general is nonsymmetrical, the experimental results should be fitted by the combination [9, 10]:

$$\tilde{\varphi}_d = D_{2\beta}|\tau|^{2\beta} + D_{1-\alpha}|\tau|^{1-\alpha} + D_1|\tau| + \dots, \quad (5)$$

where  $\beta$  is the critical exponent for the CC in terms temperature-density. The appearance of such singularity in the diameter is trivial if  $\varphi$  is a nonlinear function of some initial (laboratory) order parameter. The appearance of

the  $\tau^{2\beta}$ -singularity for the number density is partly surprising. The density is the statistical average of the simple microscopic field of the microscopic density and is nothing but the unary distribution function. This means that the density can be considered as the simplest irreducible quantity in case of the liquid-vapor CP. So if the  $2\beta$  anomaly exists for this quantity then the question about the nature of  $\tau^{2\beta}$ -singularity of the density is deeper and does not reduce to trivial algebraic relations between the thermodynamic averages.

The revival of interest to the problem of  $|\tau|^{2\beta}$ - term is connected with the complete scaling proposed in [11]. This approach is based on the supposition that all three thermodynamic fields temperature  $\tau$ , the chemical potential  $\tilde{\mu} = (\mu - \mu_c)/\mu_c$  and the pressure  $\tilde{p} = (P - P_c)/P_c$  are mixed equally. Then it is easy to show that  $\tilde{n}$  is a nonlinear function of the average of the scaling fields which represent two strongly fluctuating quantities. As a result, the appearance of the  $|\tau|^{2\beta}$ - term in Eq. (5) is caused by the nonlinear algebraic dependence between  $\tilde{n}$  and the average of the order parameter. Numerous application of this approach are given in [12–15]. In particular, in complete scaling approach the order parameter for the molecular liquids is the nonlinear combination of the density field and the density of the entropy [16]. The density of the entropy is weakly fluctuating field but the density field fluctuates more strongly.

From another point of view the problem of the singular terms in Eq. (5) is solved in [17, 18] on the basis of so called the canonical scaling. The last is the synthesis of the scaling approach and the canonical formalism, developed in the catastrophe theory [19]. In these works the regular procedure for the construction of the fluctuation Hamiltonian for liquids, which has the Ising-like form, is developed. Note, that the Ising-like Hamiltonian coincides with that given by the standard canonical form (see [20]). As will be shown below it corresponds to the thermodynamic potential with the only one vanishing eigenvalue of the stability matrix for the Gibbs potential. The CC for liquids and solutions in the canonical variables is fully symmetrical. One can say that the canonical order parameter can be considered as the optimal one. The asymmetry of the CC appears only if one returns to the laboratory variables. The evident relations between the canonical and laboratory order parameters as well as between the canonical and laboratory fields are established. The distinctive peculiarity of these relations is their nonlinear character. Nevertheless, in contrast to the complete scaling approach the canonical one operates with two fluctuating fields and uses the nonlinear

transformation rather for the field variable of the order parameter than the nonlinear transformation for its average value [18].

The motivation of this work is the search for the unifying Hamiltonian formulation of the problem of the asymmetry suitable for the determination of the proper order parameter in case of two fluctuating fields one of which fluctuates less than the other.

## 2. Gibbs potential analysis

Now we discuss briefly how the order parameter  $\varphi$  and the field  $h$  conjugated to it, as well as the value of  $r$  in Eq. (1) are connected with the expansion of the fluctuational deviation for the Gibbs potential  $g(n, s)$  near the critical point:

$$\delta g = \frac{1}{2}a_{2,0}\varphi^2 + \frac{1}{2}a_{0,2}\zeta^2 + \frac{1}{3}a_{3,0}\varphi^3 + \frac{1}{3}a_{2,1}\varphi^2\zeta + \frac{1}{3}a_{1,2}\varphi\zeta^2 + \frac{1}{3}a_{0,3}\zeta^3 + \frac{1}{3}a_{4,0}\varphi^4 + \dots \quad (6)$$

Here

$$a_{2,0} = \left. \frac{\partial \mu}{\partial n} \right|_T - \frac{(\partial T / \partial n|_s)^2}{\partial T / \partial s|_n}, \quad a_{0,2} = \left. \frac{\partial T}{\partial s} \right|_n = \frac{T}{c_v} \quad (7)$$

$$\varphi = n - n_c, \quad \zeta = s - s_c + \frac{c_v}{T} \partial T / \partial n|_s (n - n_c),$$

where  $\mu$  is the chemical potential,  $c_v$  is the heat capacity,  $n$  and  $s$  are the density and entropy correspondingly, the subscript “c” denotes their values at the critical point.

Usually it is taken into account that only one of two coefficients  $a_{2,0}$  and  $a_{0,2}$  in (6) vanishes at the critical point. The supposition

$$a_{2,0} = \left. \frac{\partial \mu}{\partial n} \right|_T \rightarrow 0, \quad T \rightarrow T_c. \quad (8)$$

corresponds to the situation when only the fluctuations of the density become anomalously large. Note that in the framework of the thermodynamic fluctuation theory the second coefficient  $a_{0,2} \neq 0$ . Indeed, in the vapor phase  $c_v$  takes the finite value and the transition to liquid state is accompanied by the addition of the only degree of freedom (the order parameter), which leads to the increase of  $c_v$  on  $\frac{1}{2}k_B$ .

Since  $a_{0,2} \neq 0$ , the fluctuations of  $\zeta$  are bounded and we can neglect them thus reducing (6) to the standard Landau expansion:

$$\delta g_L = \frac{1}{2}a_{2,0}\varphi^2 + \frac{1}{3}a_{3,0}\varphi^3 + \frac{1}{4}a_{4,0}\varphi^4 + \frac{1}{5}a_{5,0}\varphi^5 + \dots \quad (9)$$

In fact the local part of Eq. (1) is nothing but the local form of Eq. (9) truncated to the minimal polynom sufficient to describe the reconstruction of the minima which represent the coexisting phases.

The transformation from the infinite series (9) to the canonical form (1) is discussed in details in [18, 20]. In that case when  $c_v$  is bounded, the canonical form for the local part of the fluctuation Hamiltonian takes the form:

$$h_{loc}(\psi) = \delta g_L|_{\varphi \rightarrow \varphi(\psi)} = \frac{1}{4}g\psi^4 + \frac{1}{2}r\psi^2 + h_\psi\psi \quad (10)$$

The canonical order parameter  $\psi$  is the nonlinear function of initial variable  $\varphi$ :

$$\psi = \varphi + \frac{1}{2}\gamma_2\varphi^2 + \frac{1}{2}\gamma_3\varphi^3 + \dots$$

Explicit expressions for  $g, r$  and  $h_\psi$  as well as for the coefficients  $\gamma_n$  can be found in [21].

However, in many cases the applicability region of the thermodynamic fluctuation theory or the mean-field approximation is absent. Argon can serve as the simplest example of such a kind. It is evident from the behavior of its isothermal compressibility. In other words the Ginsburg temperature for argon and many other liquids is close to unity  $\tau_{Gi}(Ar) \sim (0.1 \div 0.3)$  [22]. It means that the behavior of the heat capacity  $c_v$  is determined by fluctuation effects. Therefore, fluctuation effects cannot be ignored and they lead to the vanishing of the quantity  $T/c_v$ , which is the second eigenvalue of the quadratic form in Eq. (6). In such a case the canonical form for the local part of the fluctuation Hamiltonian should be generalized since both variables  $\varphi$  and  $\zeta$  should be considered as the strongly fluctuating ones.

The new version of the fluctuational Hamiltonian will be able to reflect more exactly the relative role of mechanical and thermal variables, which are used for the description of the critical behavior. At that, if an order parameter is modeled by a mechanical variable, the auxiliary field in the fluctuational Hamiltonian is given by caloric one and vice versa. In particular, the specific volume as the order parameter is completed by the specific entropy. Taking into account of this variable is especially important for complex liquids,

molecules of which rotate, can form H-bonds and have internal degrees of freedom excited in the thermal motion, as well as for multicomponent solutions. Since fluctuations of the specific volume and specific entropy are not orthogonal, the increase of the role of caloric effects should be accompanied by a growth of the coexistence curve asymmetry. In connection with the last problem, it is necessary to note that the asymmetry of coexistence curves arises not only due to caloric effects. Another mechanism is caused by hard core effects. Their manifestation in complex liquids is similar to that for simple liquids. Therefore in this paper our attention will be mainly focused on the inclusion of the caloric effects into the fluctuational Hamiltonian.

Therefore the fluctuational Hamiltonian should be built on the basis of the canonical form for the thermodynamic potential which is consistent with the fact of the existence of two strongly fluctuating fields. Another support for such conjecture is given by the two-dimensional lattice models where the requirement of the conformal symmetry leads to the two independent strongly fluctuating fields [23, 24]. From here and the very general isomorphism principle it follows that the bare fluctuation Hamiltonian for liquids should also contain two independent order parameters.

### 3. Fluctuation Hamiltonian of the system

The local part of the fluctuation Hamiltonian for a system, for which two eigenvalues  $a_{2,0}$  and  $a_{0,2}$  of the stability matrix tend to zero at the critical point, in accordance with the catastrophe theory must be built on the basis of  $D_5$  catastrophe [21]:

$$\delta g|_{\varphi \rightarrow \psi(\varphi, \zeta), \zeta \rightarrow \sigma(\varphi, \zeta)} = \frac{1}{4} \psi^4 + b \psi \sigma^2 + \frac{1}{2} r \psi^2 + \frac{1}{2} u \sigma^2 + h_\psi \psi + h_\sigma \sigma, \quad (11)$$

where  $\psi$  and  $\sigma$  are the corresponding canonical variables which are the non-linear functions of the initial variables  $\varphi$  and  $\zeta$ . In view of the results of Ref. [18] the parameter of the asymmetry coupling  $b$  canonically represents the degree of the asymmetry of the initial Hamiltonian.

The fluctuational Hamiltonian consists of two parts:

$$\mathcal{H} = H_{loc} + H_{qloc},$$

the local part  $H_{loc}$

$$H_{loc} = \int \delta g(\psi(\mathbf{r}), \sigma(\mathbf{r})) d\mathbf{r}$$

and the quasilocal part  $H_{qloc}$ . For the latter we use common quadratic gradient approximation. In accordance with Eq. (11) the local part of the fluctuational Hamiltonian has the form:

$$H_{loc}[\psi(\mathbf{r}), \sigma(\mathbf{r})] = H_{loc}[\psi(\mathbf{r})] + H_{loc}[\sigma(\mathbf{r})] + H_{int}[\psi(\mathbf{r}), \sigma(\mathbf{r})] , \quad (12)$$

with

$$H_{loc}[\psi(\mathbf{r})] = \int d\mathbf{r} \left[ -h_\psi \psi + \frac{1}{2} r \psi^2 + \frac{1}{4} g \psi^4 \right] , \quad (13)$$

$$H_{loc}[\sigma(\mathbf{r})] = \int d\mathbf{r} \left[ -h_\sigma \sigma + \frac{1}{2} u \sigma^2 \right] , \quad (14)$$

$$H_{int}[\psi(\mathbf{r}), \sigma(\mathbf{r})] = \int d\mathbf{r} b \psi \sigma^2 . \quad (15)$$

Here  $\psi(\mathbf{r})$  and  $\sigma(\mathbf{r})$  are the fluctuating fields. In accordance with Eq. (6)  $\psi(\mathbf{r})$  can be identified with the density while  $\sigma(\mathbf{r})$  is the combination of the density and the entropy fluctuations. The local part of the Hamiltonian should be completed with the relevant gradient terms. They are

$$H_{nloc}[\psi(\mathbf{r})] = \int \frac{1}{2} (\nabla \psi(\mathbf{r}))^2 d\mathbf{r} , \quad (16)$$

$$H_{nloc}[\psi(\mathbf{r})] = \int \frac{c_\psi \sigma}{2} \nabla \psi(\mathbf{r}) \cdot \nabla \sigma(\mathbf{r}) d\mathbf{r} . \quad (17)$$

We did not include the quadratic term  $(\nabla \sigma)^2$  because as we show below within the dimensional analysis it is irrelevant.

### 3.1. Simple dimensional analysis

Here we perform the analysis of the Hamiltonian (12) introduced above using the simple scaling [25]. From the elementary analysis of dimensions and the fact that the main contribution to the coefficient  $u$  are caused by the fluctuations of the free field  $\varphi$  it follows that its dimension is  $\Delta_u^{(0)} = \Delta_g^{(0)} = 4 - d = \epsilon$ . The character of the temperature dependence of  $r$  does not change in comparison with (1), so  $\Delta_r^{(0)} = 2$  and  $r = r_d \tau$ . Also it is obvious that  $\Delta_\sigma^{(0)} = 2\Delta_\psi^{(0)} = d - 2$ . Thus for the conjugated field  $h_\sigma$  we have  $\Delta_{h_\sigma}^{(0)} = d - \Delta_\sigma^{(0)} = 2$ , thus it is nothing but the canonical temperature variable. The field  $h_\psi$  obviously plays the role of the canonical chemical potential and the condition  $h_\psi = 0$  determines the coexistence line. The scaling dimension of  $b$

- the strength of asymmetric interaction is  $\Delta_b^{(0)} = \frac{3}{2} \left( \frac{10}{3} - d \right)$ , which becomes relevant below  $d = \frac{10}{3}$  and thus equivalent to the quintic  $\psi^5$  asymmetrical term in the standard consideration [26]. The gradient term in Eq. (17) has the same dimension as the asymmetric term  $\varphi (\nabla\psi)^2$ , which should be taken into account along with the quintic coupling [27]. The term  $(\nabla\sigma)^2$  can be omitted because it is irrelevant (with dimension  $\Delta_{\nabla\sigma}^{(0)} = 2 - d = -2 + \epsilon$ ).

For the Ising model because of the symmetry  $\psi \rightarrow -\psi$ ,  $b = c_{\psi\sigma} = 0$  and the fields  $\psi$  and  $\sigma$  decouple.

Previous consideration of the classical scaling dimensions obviously allows to identify  $\sigma$  with the field :  $\psi^2(\mathbf{x})$  :. With account of the fluctuations the dimensions are renormalized  $\Delta_\psi = \Delta_\psi^{(0)} + \frac{\eta}{2}$  and  $\Delta_\sigma = \Delta_\sigma^{(0)} + 2 - \frac{1}{\nu}$  so that  $\Delta_{h_\sigma} = 1/\nu$  and indeed  $h_\zeta$  is a temperature field. Here  $\nu$  is the critical exponent of the correlation length and  $\eta$  is the Fisher's critical exponent of the anomalous dimension [28]. The dimension of the parameter  $u$  is  $\Delta_u = \frac{2}{\nu} - d = \frac{\alpha}{\nu}$ . This leads to the conclusion that indeed  $u \propto \tau^\alpha$ , i.e. asymptotically it is the inverse value of the specific heat.

#### 4. Fluctuation Hamiltonian for binary solution

In this Section we briefly discuss the specificity of the fluctuation Hamiltonian in binary solutions. The method of consideration is naturally generalized for arbitrary multi-component solutions.

Let us consider the binary solution, for which the total number of particles remains to be constant. In this case the thermodynamic state of the system is set by the temperature and pressure as well as the difference of the chemical potentials of components:  $\mu = \mu_2 - \mu_1$ . Considering  $\mu$  as a function of specific volume  $v$ , entropy and concentration  $x$  we can write the following expression for the increment of the chemical potential near its minimal value:

$$\delta^2\mu = \frac{1}{2} \left[ \frac{M_3}{M_2} \delta x^2 + \frac{M_2}{M_1} (\delta x + c\delta v)^2 + M_1 (\delta x + a\delta s + b\delta v)^2 \right] + \dots \quad (18)$$

Here  $M_i$ ,  $i = 1, 2, 3$ , are the main minors of the matrix:

$$\hat{M} = \begin{pmatrix} \partial T / \partial s & \partial T / \partial v & \partial T / \partial x \\ \partial P / \partial s & \partial P / \partial v & \partial P / \partial x \\ \partial \mu / \partial s & \partial \mu / \partial v & \partial \mu / \partial x \end{pmatrix}.$$



In fact, the diagonal form (18) is naturally obtained by the Lagrange method.

The coefficients  $a$ ,  $b$  and  $c$  are some combinations of the elements of  $\hat{M}$ .

It is not difficult to verify that near the mixing critical point:

$$\frac{M_3}{M_2} \sim \left. \frac{\partial \mu}{\partial x} \right|_{P,T} \quad \text{and} \quad \frac{M_2}{M_1} \sim \frac{T}{c_{\mu v}}$$

Since  $M_1 = \frac{T}{c_{xv}}$  and  $c_{xv}$  takes the finite value for binary solution the fluctuations of the combination  $\delta u = \delta x + a\delta s + b\delta v$  are bounded and the contribution of corresponding term in Eq. (18) can be omitted.

Let us compare (18) with the analogous increment of the chemical potential for one-component liquid near its vapor-liquid critical point. In this case

$$\delta^2 \mu = \frac{1}{2} \left[ \frac{M_2}{M_1} \delta v^2 + M_1 (\delta s + a\delta v)^2 \right] + \dots,$$

where

$$\hat{M} = \begin{pmatrix} \partial T / \partial s & \partial T / \partial v \\ \partial P / \partial s & \partial P / \partial v \end{pmatrix},$$

and  $\frac{M_2}{M_1} = -\left. \frac{\partial P}{\partial v} \right|_T$  and  $M_1 = \frac{T}{c_v}$ .

As we see, the characters of the near-critical behavior of  $\delta^2 \mu$  for binary solutions and one component liquids are fully identical. Therefore we conclude that critical phenomena in them are isomorphic, i.e. their fluctuation Hamiltonians have the same form.

## 5. Conclusions

We have performed the stability analysis of the thermodynamic potential for the molecular systems with the critical point where  $\tau_{Gi}$  is not small  $\tau_{Gi} \gtrsim 0.1$ . Such situation means that there is no crossover region to the mean-field behavior so the canonical form for the fluctuational Hamiltonian include two independent fluctuating fields. Both fields are strongly fluctuating but one of them has the strongest singularity caused by the slowest decay of its correlator. The proposed canonical form of the fluctuational Hamiltonian is constructed on the basis of  $D_5$  catastrophe and contain asymmetrical term which describes the coupling between these fields. If the contribution of less fluctuating field is neglected we get the standard Landau-Ginzburg-Wilson Hamiltonian. The facts that  $\tau_{Gi}$  is not small and the leading correction to

the quadratic part (random phase approximation) is determined by  $\psi^4$  term allow to conclude about global cubic character of the binodal. This is in accordance with the global isomorphism proposed in Ref. [29].

Simple scaling analysis shows that one of the field can be identified with the density-like one while another field corresponds to the fluctuations of the entropy. We hope that the proposed canonical form can serve as the basic fluctuational Hamiltonian which describes the asymmetry effects characteristic for the real fluids more adequately. The problem of derivation of (12) on the basis of microscopic Hamiltonian can be performed within the canonical approach [18, 20].

The physical reasonings for the appearance of two fluctuating fields are connected with the account of the hard core effects in the microscopic Hamiltonian. Usually the microscopic Hamiltonian is divided into short-range and long-range parts due to the corresponding division of the interaction potential into repulsive and attractive ones. The repulsive part is usually integrated over and the fluctuational part depending only on the density fluctuations appears (see e.g. Refs. [3, 4]). The asymmetry of the coexistence curves for real liquids arises due to the breaking of the particle-hole symmetry for the lattice gas. This symmetry is first of all violated because of different role of the hard core effects in liquid and vapor phases. It is also violated by different manifestation of caloric effects in coexistence phases.

It is necessary to stress that the canonical fluctuation Hamiltonian (12) of liquids is not isomorphic to that for the Lattice Gas or equivalently for the Ising model, since the interaction Hamiltonian (15) is an odd function of the order parameter:  $H_{int}[-\psi(\mathbf{r}), \sigma(\mathbf{r})] = -H_{int}[\psi(\mathbf{r}), \sigma(\mathbf{r})]$ . We can speak about isomorphism between them only if  $H_{int}[\psi(\mathbf{r}), \sigma(\mathbf{r})]$  is negligibly small. The results of Ref. [18] allow to connect the parameter of the asymmetry coupling  $b$  with the asymmetry of the initial Hamiltonian on the basis of the model for the equation of state for the real molecular fluids. With such model equation of state the caloric and the hard core effects can be taken into account explicitly. The detailed consideration of this question will be a subject of prospective work.

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